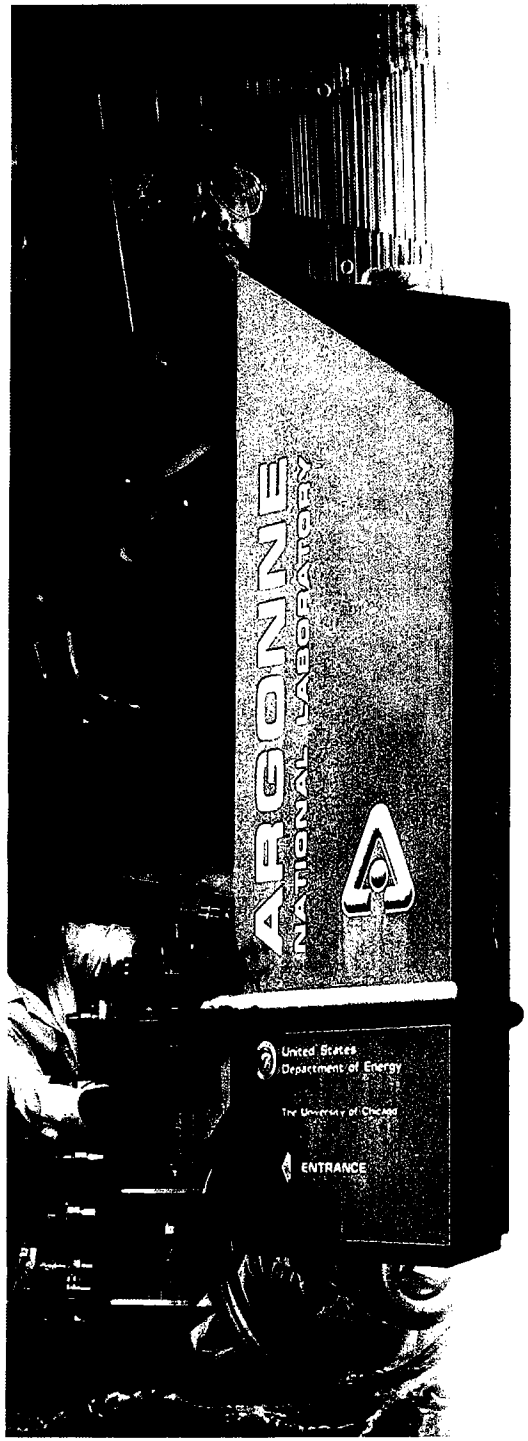


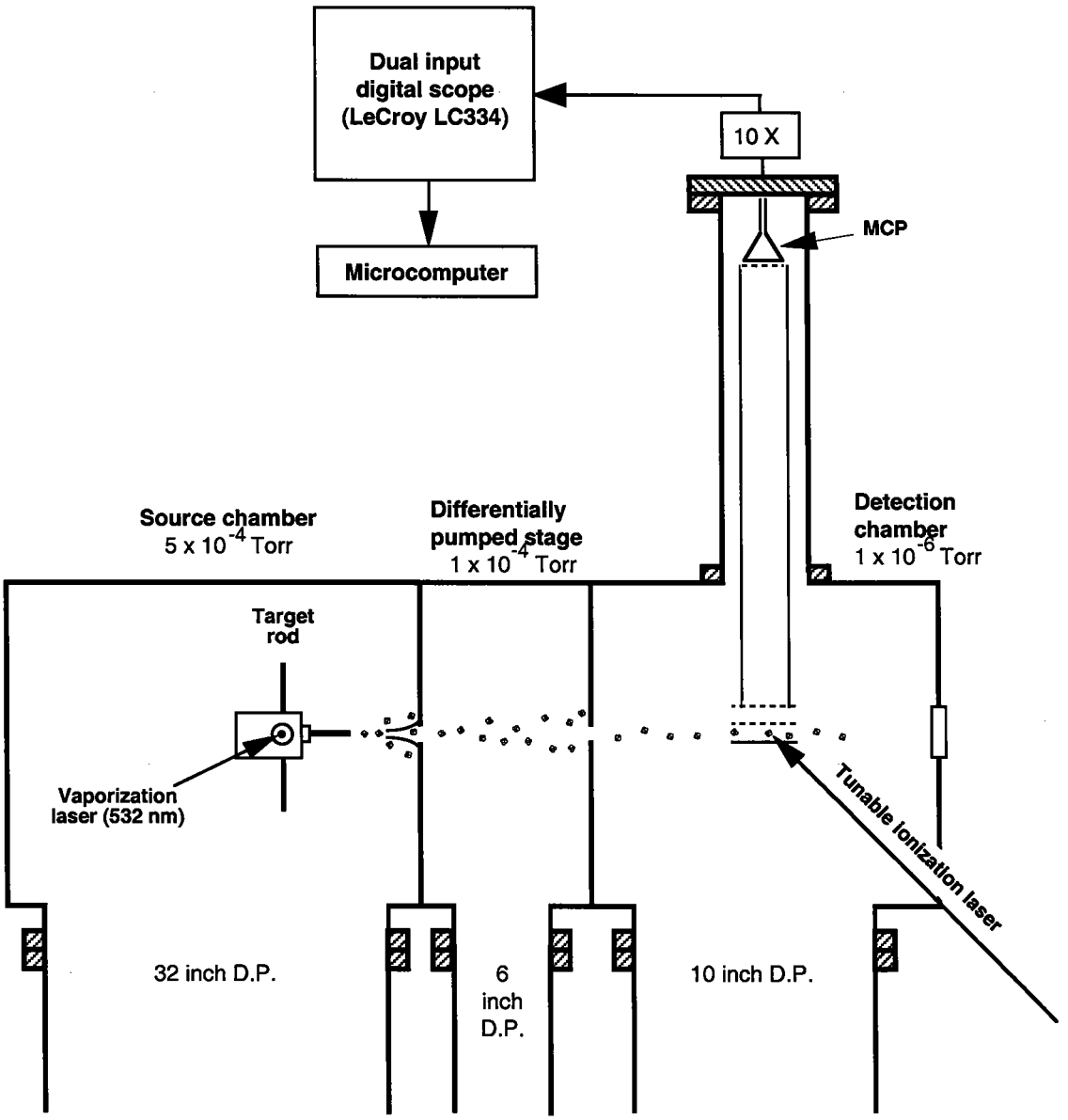
Transient Species in Beams: Photoabsorption by Metal Clusters and Complexes

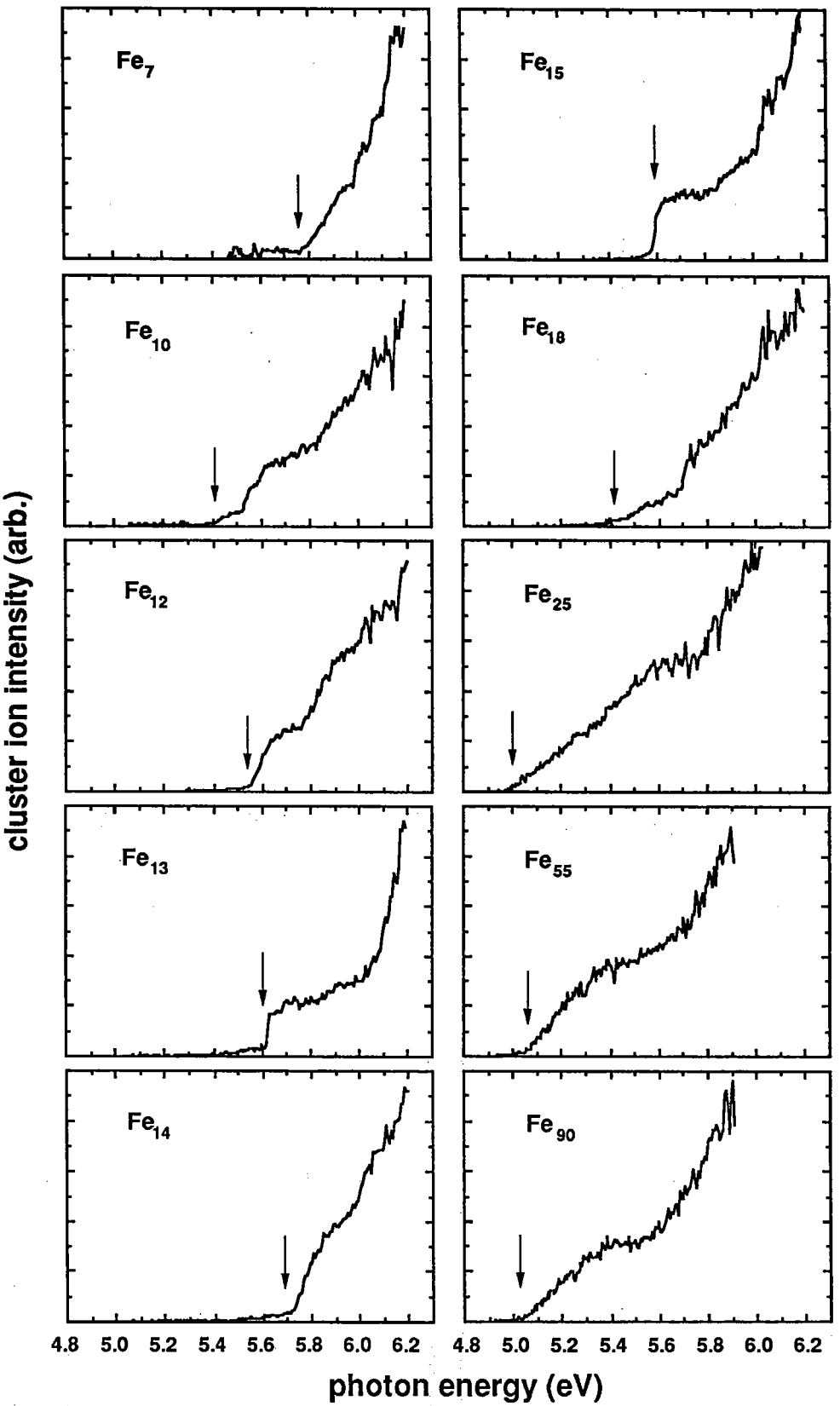
Mark B. Knickelbein
Chemistry Division
Argonne National Laboratory

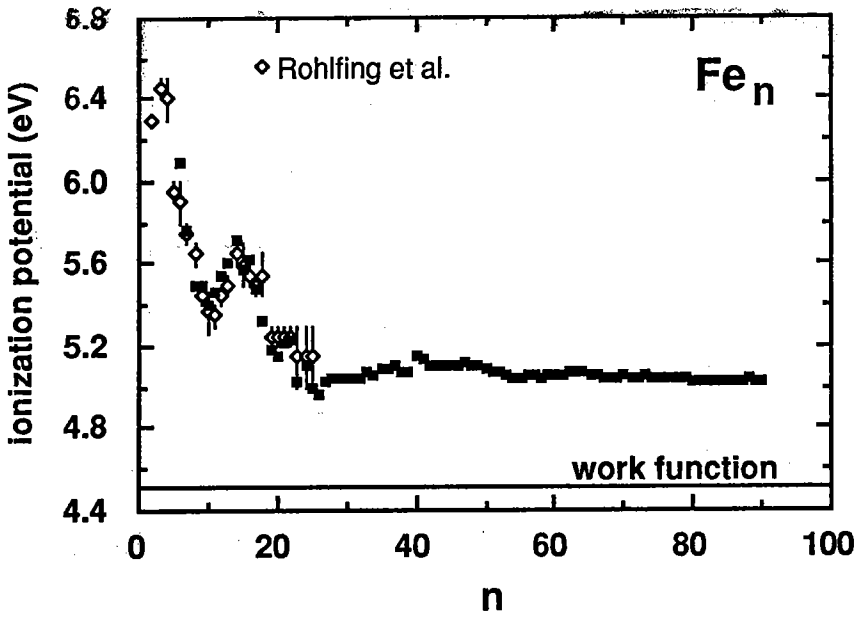
Argonne National Laboratory

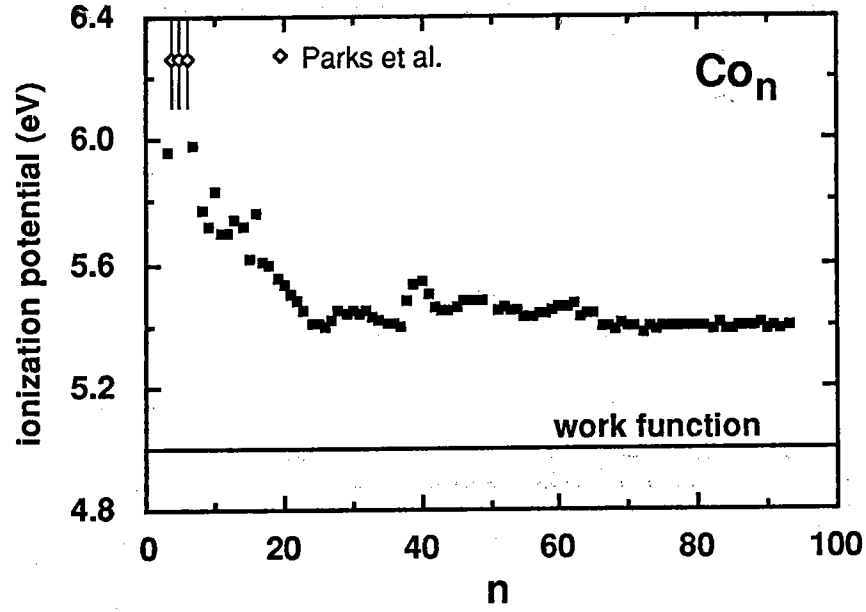
Office of Science
U.S. Department of Energy

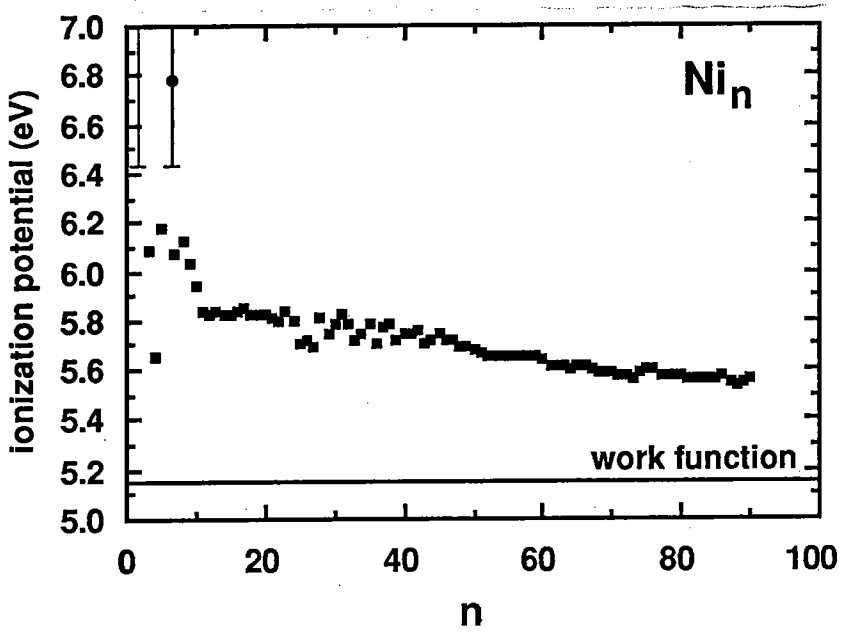
A U.S. Department of Energy
Office of Science Laboratory
Operated by The University of Chicago

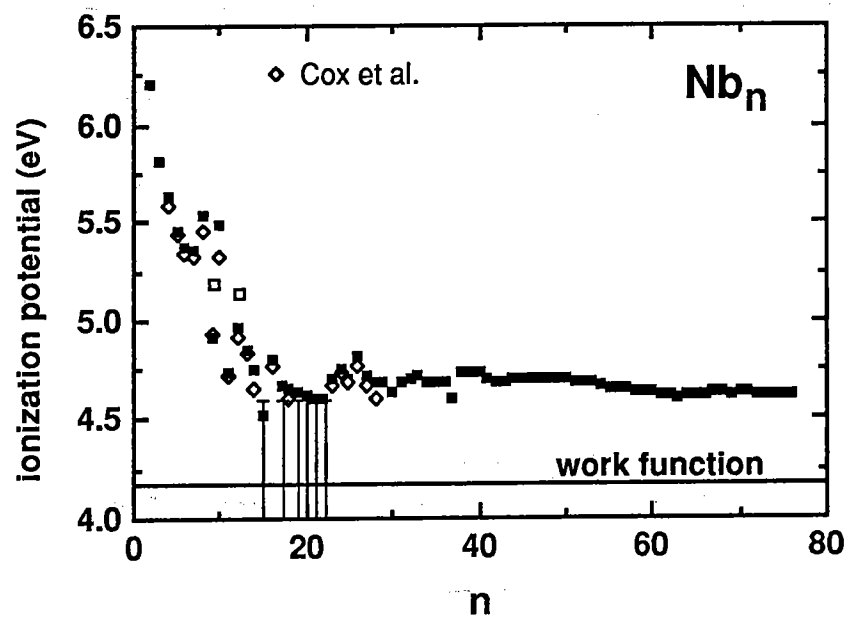

Dual input
digital scope
(LeCroy LC334)
10 X
MCP
Microcomputer
Source chamber
5 x 10-4 Torr
Differentially
pumped stage
1 x 10-4 Torr
Detection
chamber
1 x 10-6 Torr
Target
rod
Vaporization
laser (532 nm)
Tunable ionization laser
32 inch D.P.
6
inch
D.P.
10 inch D.P.

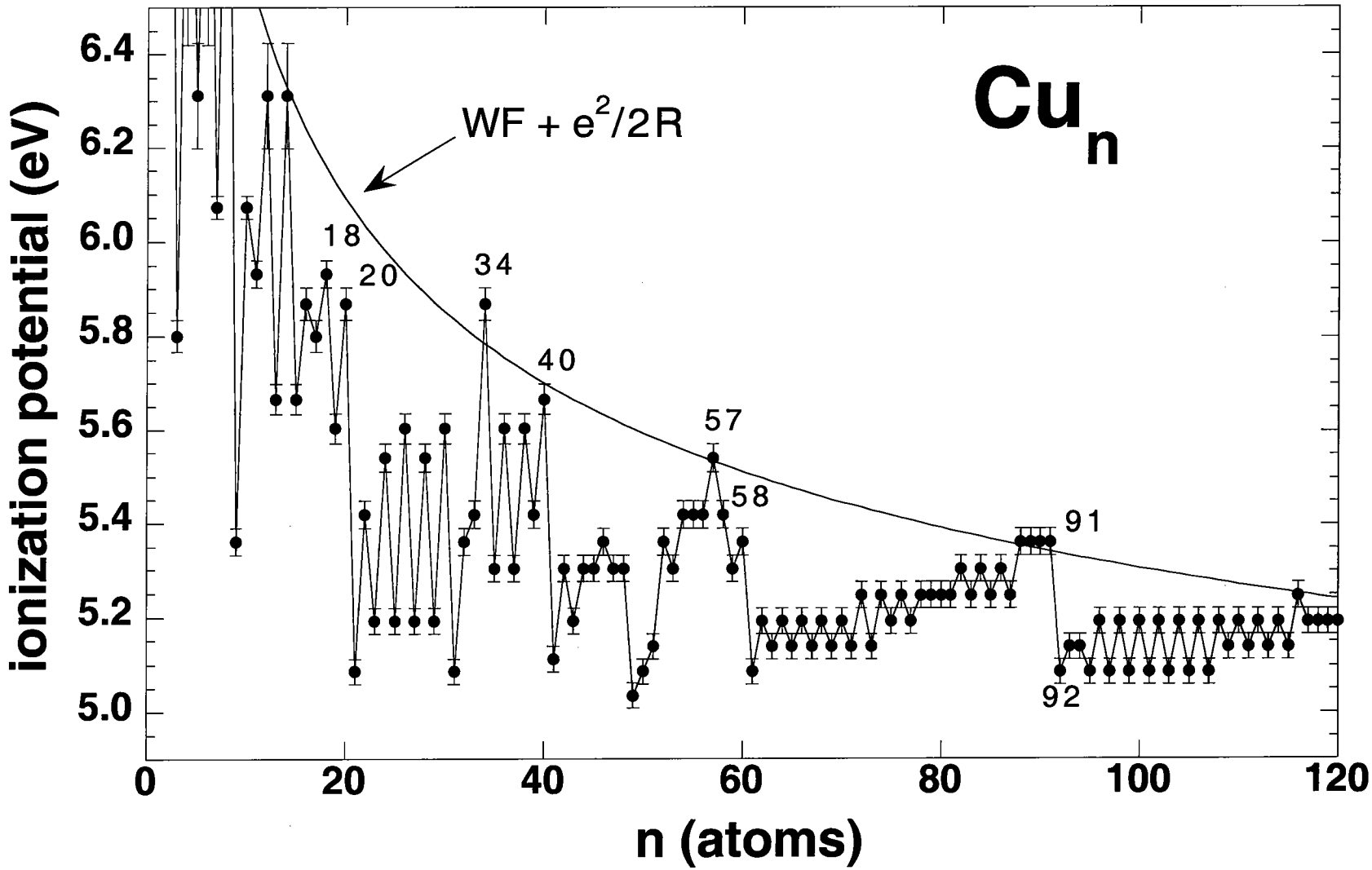

Fe7
Fe15
Fe10
Fe18
Fe12
Fe25
Fe13
Fe55
Fe14
Fe90
cluster ion intensity (arb.)
4.8 5.0 5.2 5.4 5.6 5.8 6.0 6.2
4.8 5.0 5.2 5.4 5.6 5.8 6.0 6.2
photon energy (eV)


Rohlfing et al.
Fe_n
ionization potential (eV)
work function
n


Parks et al.
Co_n
ionization potential (eV)
work function
n


Ni_n
ionization potential (eV)
work function
n

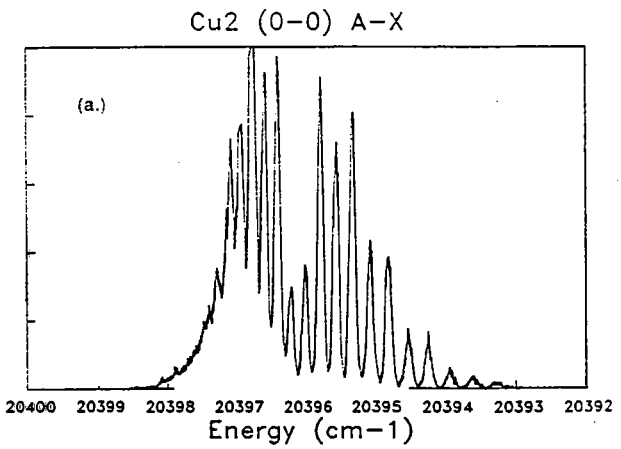

Cox et al.
Nb_n
ionization potential (eV)
work function
n

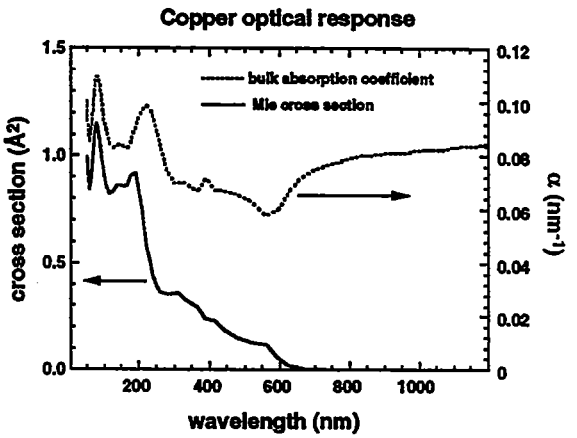

Cu n
WF + e2/2R
ionization potential (eV)
n (atoms)
6.4
6.2
6.0
5.8
5.6
5.4
5.2
5.0
0
20
40
60
80
100
120
18
20
34
40
57
58
91
92

Metal Cluster Spectroscopy

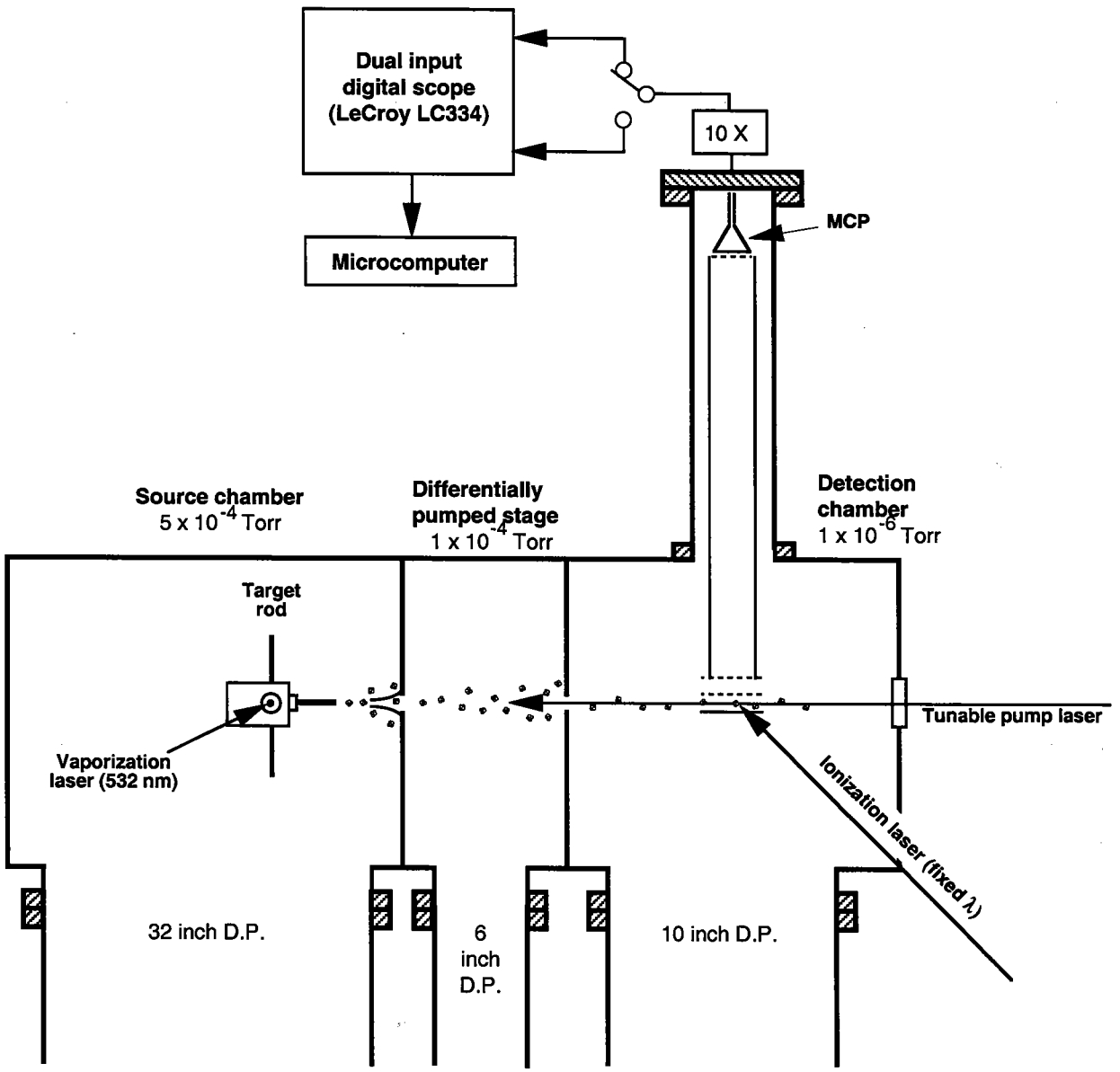
Molecules → **Clusters (to 10^3 atoms)** ← **Crystalline Solids**

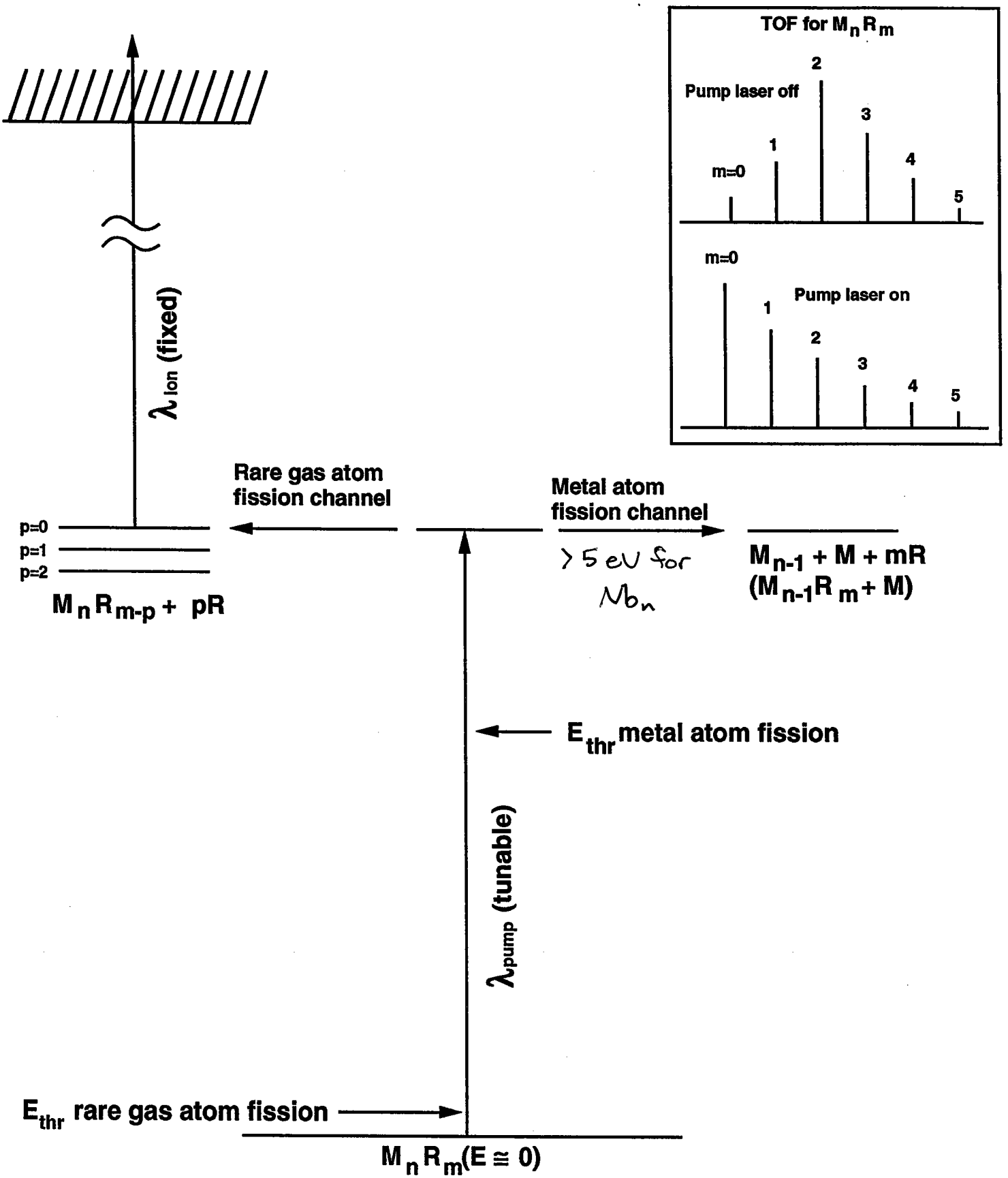
Cu_2	Cu_{40}	Cu (fcc)
Molecular spectra (Sharp, diffuse)	**?**	**Bulk absorptivity ($\alpha = 4\pi k/\lambda$)**

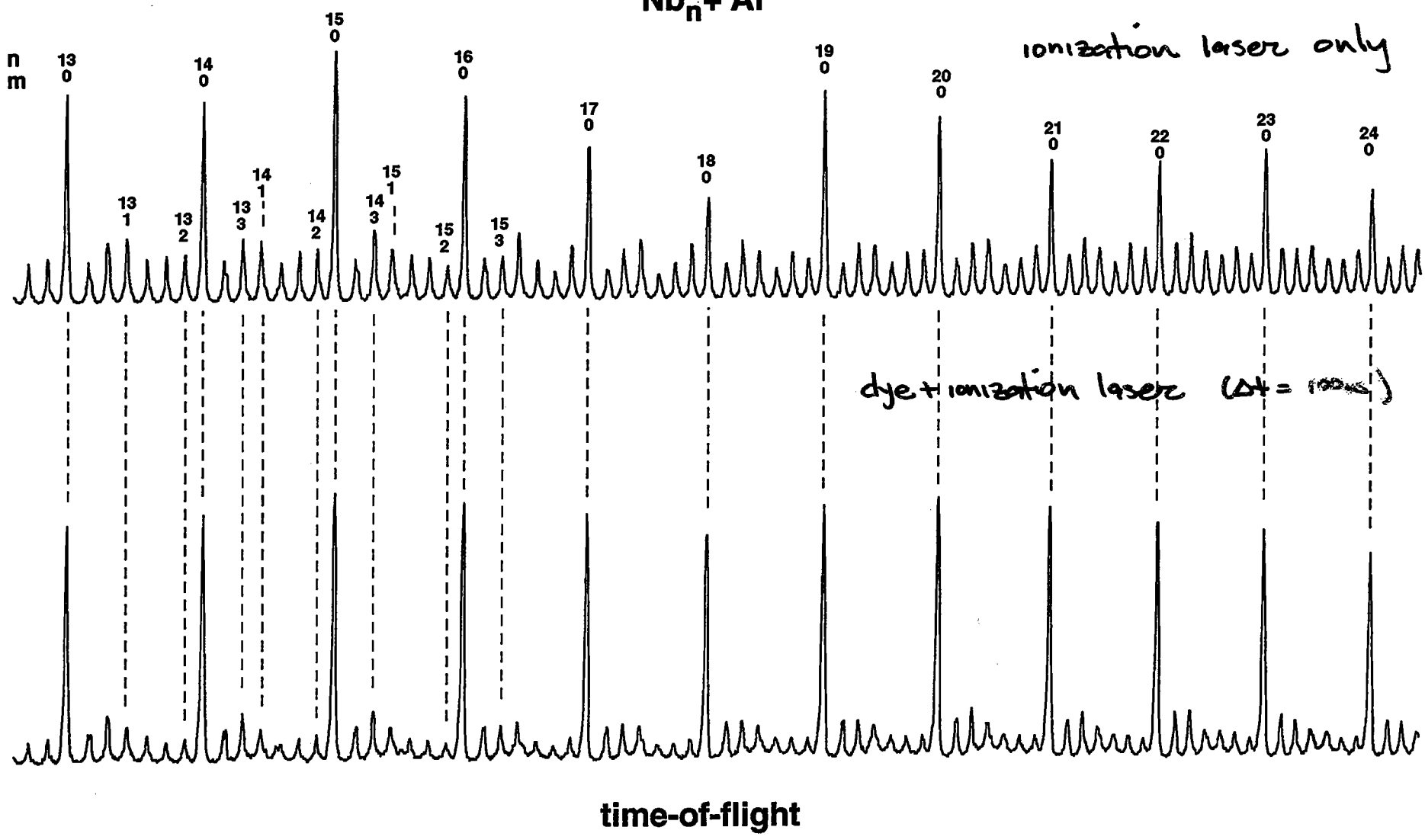


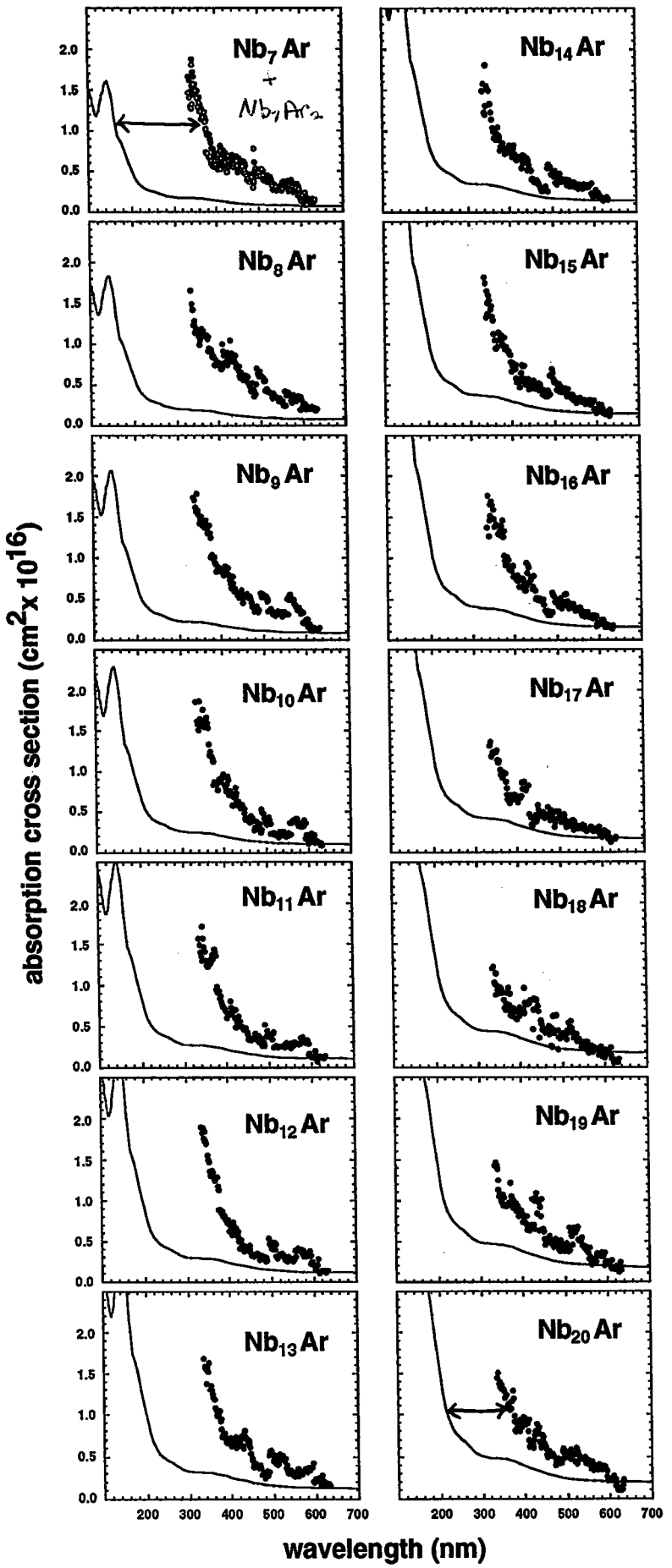


Molecular eigenstates Continuum states	**?**	**Band structure**


Dual input
digital scope
(LeCroy LC334)
10 X
MCP
Microcomputer
Source chamber
5 x 10^-4 Torr
Differentially
pumped stage
1 x 10^-4 Torr
Detection
chamber
1 x 10^-6 Torr
Target
rod
Tunable pump laser
Vaporization
laser (532 nm)
Ionization laser (fixed λ)
32 inch D.P.
6
inch
D.P.
10 inch D.P.

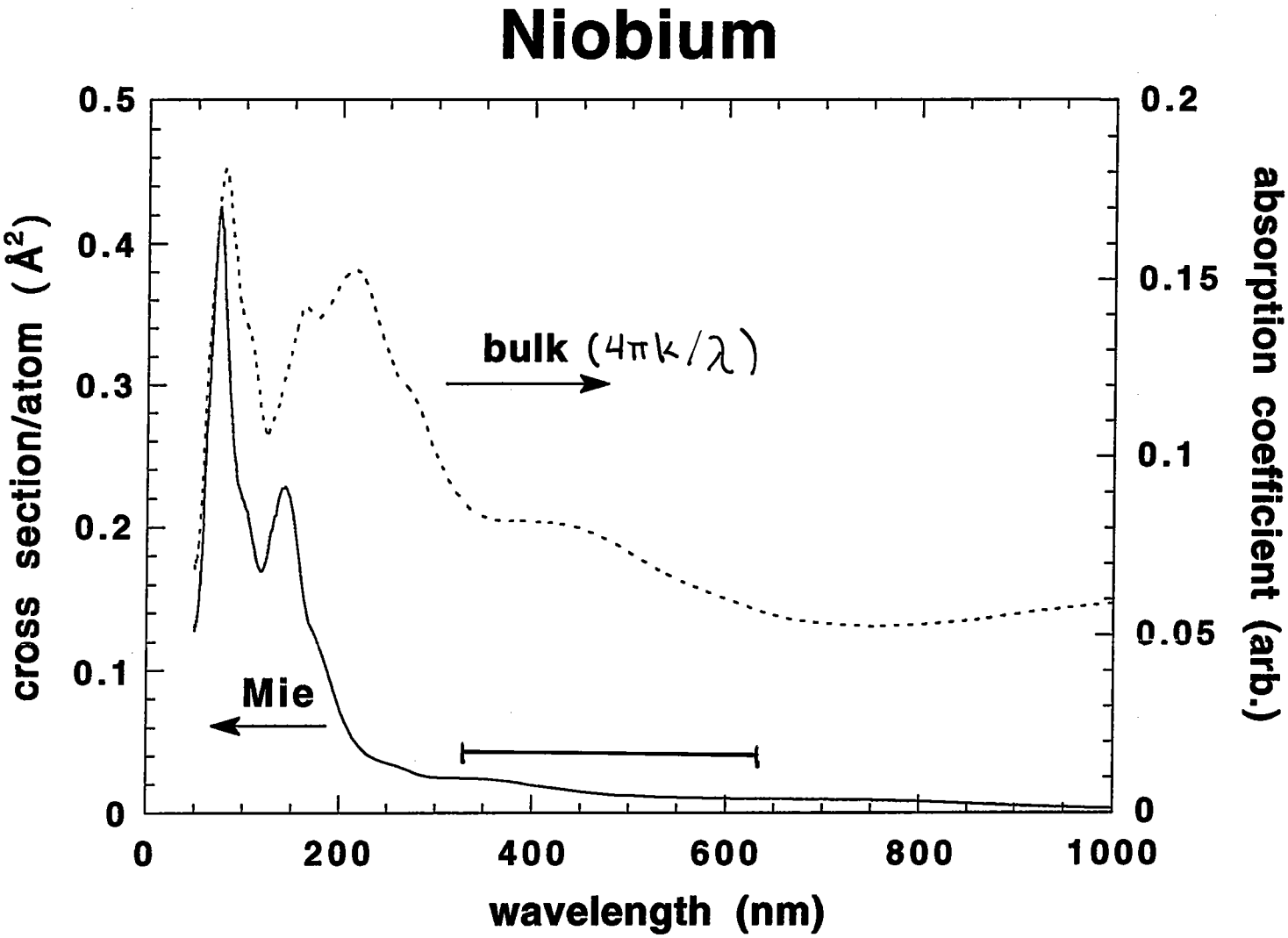

TOF for $M_n R_m$
Pump laser off
m=0
1
2
3
4
5
m=0
Pump laser on
1
2
3
4
5
λ_{Ion} (fixed)
Rare gas atom fission channel
Metal atom fission channel
> 5 eV for Mb_n
p=0
p=1
p=2
$M_n R_{m-p} + pR$
$M_{n-1} + M + mR$
$(M_{n-1} R_m + M)$
E_{thr} metal atom fission
λ_{pump} (tunable)
E_{thr} rare gas atom fission
$M_n R_m (E \cong 0)$


Nb_n+ Ar
ionization laser only
dye + ionization laser (Δt = 100ns)
n
m
13 0
13 1
13 2
13 3
14 0
14 1
14 2
14 3
15 0
15 1
15 2
15 3
16 0
17 0
18 0
19 0
20 0
21 0
22 0
23 0
24 0
time-of-flight



$$\sigma_{nie}(\lambda) \sim \frac{\varepsilon_2}{(\varepsilon_1+2)^2 + \varepsilon_2^2}$$

$\tilde{\varepsilon} = \varepsilon_1 + i\varepsilon_2$ for bulk Nb (Weaver et al.)


Niobium
0.5
0.4
0.3
0.2
0.1
0
cross section/atom (Å²)
0.2
0.15
0.1
0.05
0
absorption coefficient (arb.)
bulk (4πk/λ)
Mie
0
200
400
600
800
1000
wavelength (nm)

Opportunities in the Visible and UV

- Optical response of clusters and nanoparticles in the VUV via action spectroscopies
- Ionization energies of small clusters, complexes, and other transient species having IEs > 6.4 eV
- Pump-probe studies of cluster photofragmentation
- Electron detachment studies of clusters at high photon energies (probe deeper into valence band)

Acknowledgements

Shihe Yang
Warren Menezes
Geoff Koretsky